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Resistless Ga+ beam lithography for flexible prototyping of nanostructures

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CUPAL Nanotech Career-up Alliance
Nanotech Career-up Alliance
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Outline

- Introduction
  - **Resistless Ga^+ beam lithography**
    - Principles
    - Review and overview
- Experimental @ IISB
  - Sample processing
  - Results for Si, SiO_2 and 4H-SiC
- Summary

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Motivation

- The need for nanostructures is steadily increasing for e.g.:
  - **biomedical applications, analytics …**
  - **photonics, nanoelectronics…**

- Often, optimum dimensions and overall geometry is not known a priori
  - flexible and fast prototyping beneficial
  - focused ion beam (FIB) systems could be used directly and are often available even in research environment but only provide slow processing speed

  → **increased throughput would allow flexible and acceptably fast prototyping**

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Resistless Ga^+ beam lithography (GaRL)

- Resistless Ga+ beam lithography (GaRL) makes use of an etch rate reduction (masking effect) for Ga irradiated areas
- Ga focused ion beam systems (FIB) are used as “lithography” tool
  → **nano pattern definition capability**
- Standard etching processes are used for structure transfer into the underlying substrate
  → **(relatively) large volume removal capability**

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Resistless Ga$^+$ beam lithography (GaRL)

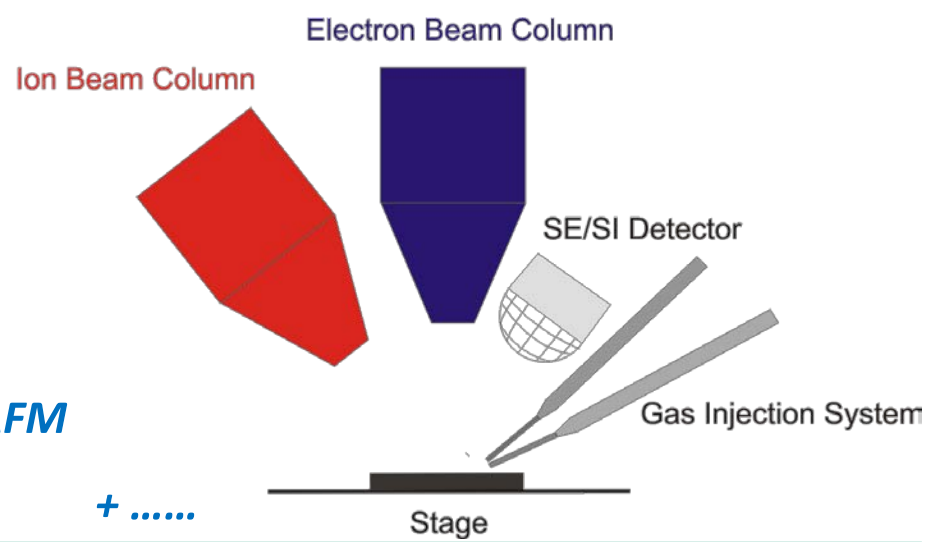
- **Focused ion beam (FIB) systems (since 70's, 80's)**
  - liquid metal ion source (LMIS)
  - often with electron beam column (SEM)
  - gas injection system (GIS)
  - different detectors

+ EDX

+ SIMS

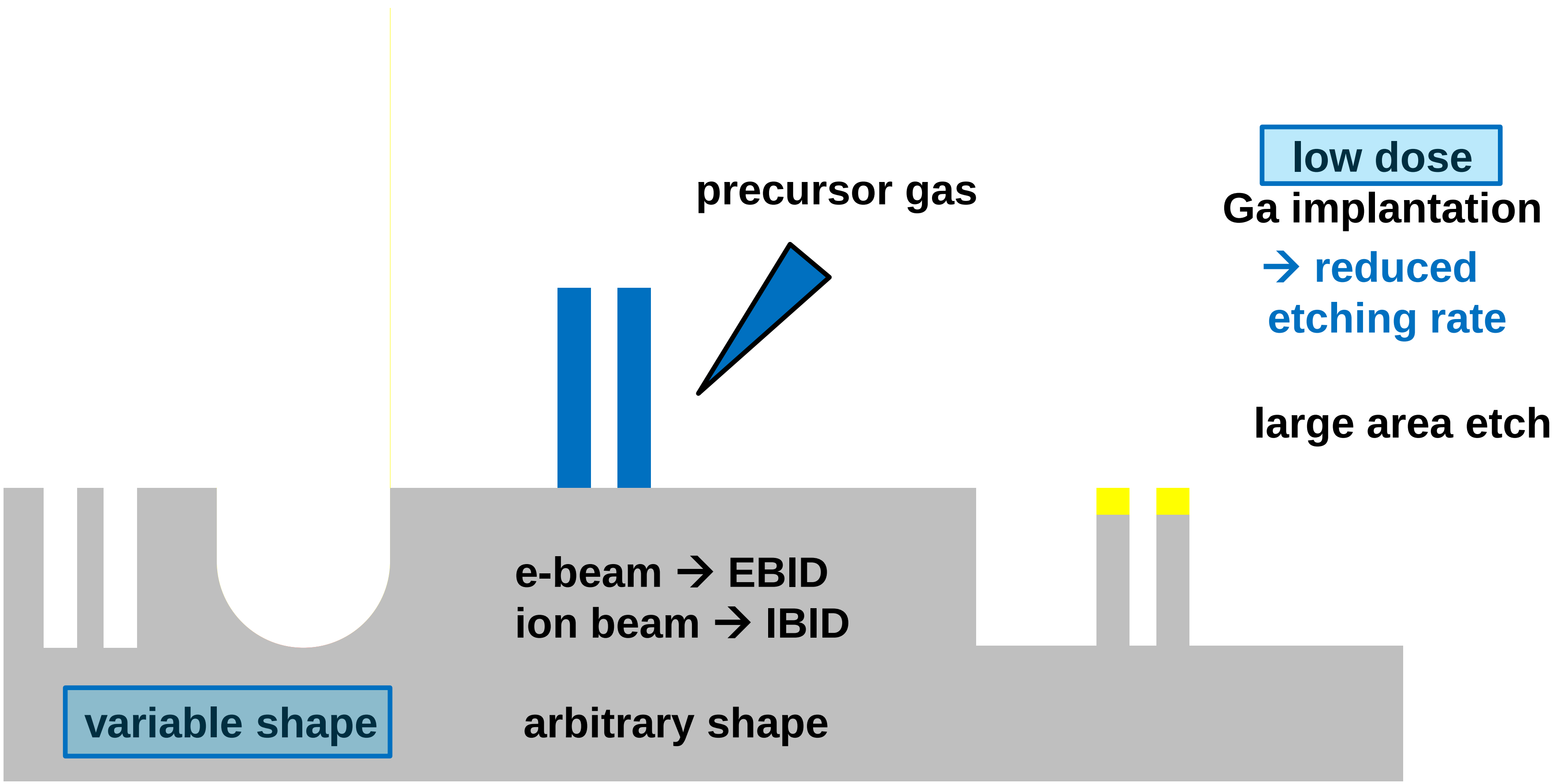
+ AFM

+ ……



FIB – fundamental modes of structure fabrication

ion milling (high dose) | **gas assisted deposition (or etching)** | **resistless Ga^+ beam lithography**



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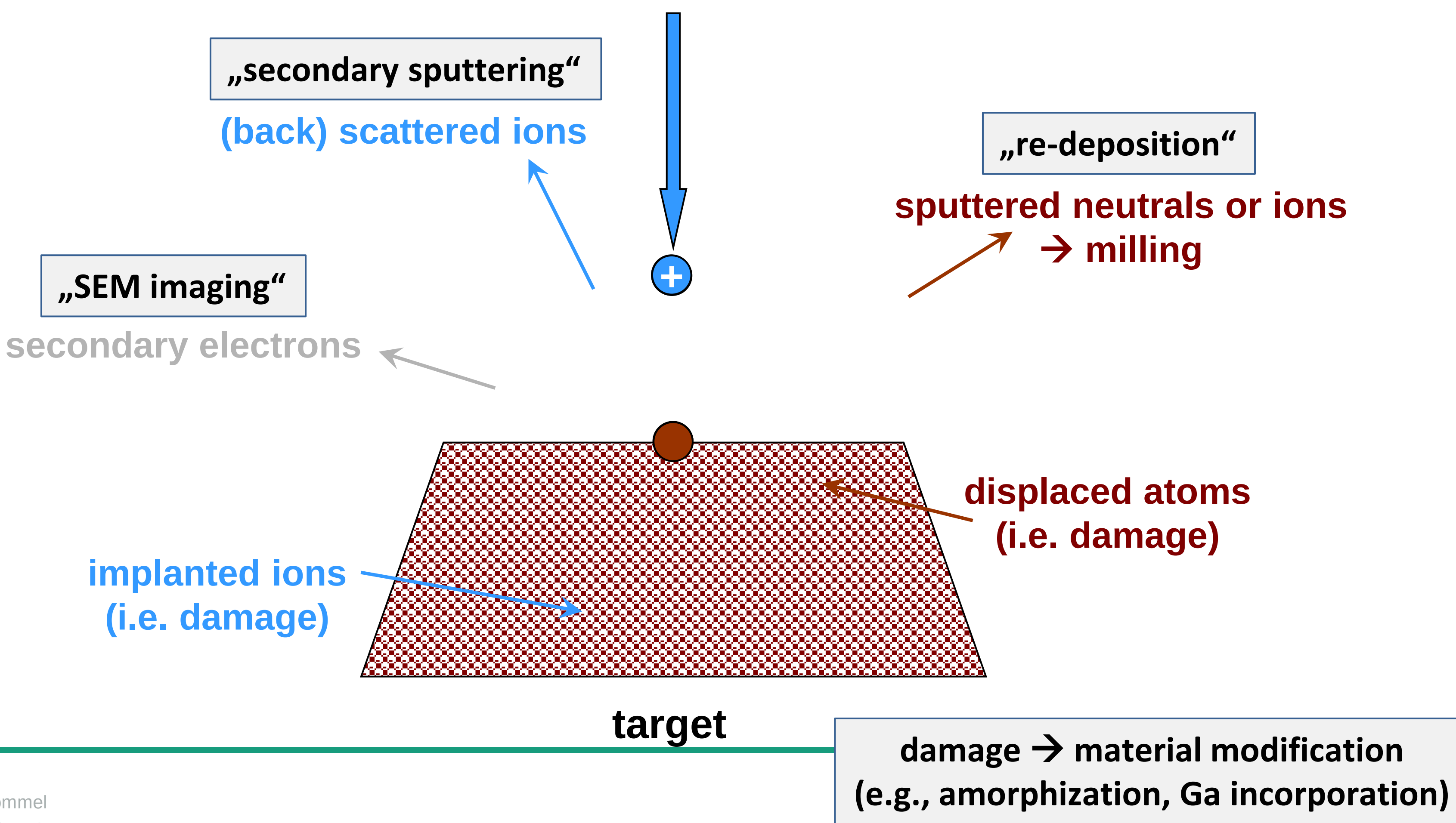
Resistless Ga$^+$ beam lithography (GaRL)

- **Ion solid interaction**



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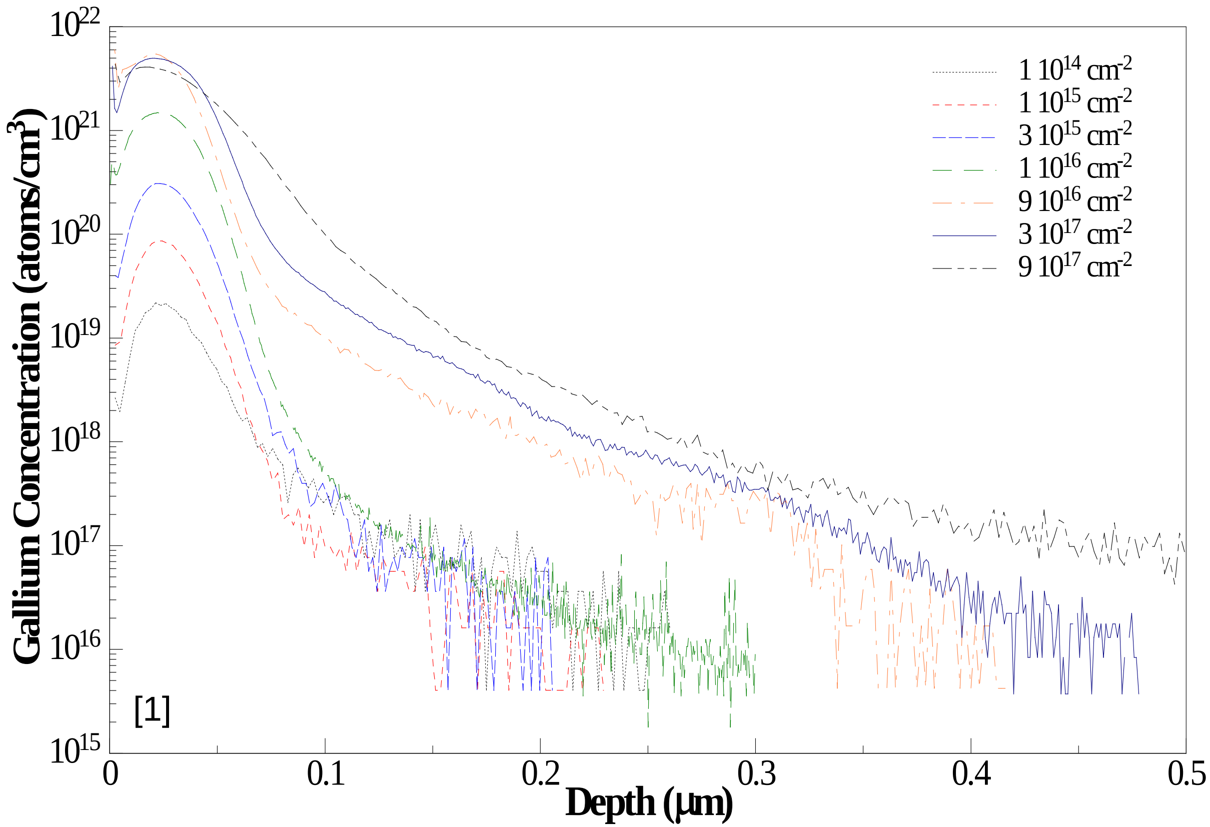
Resistless Ga^{+} beam lithography (GaRL)

- **Ga (30 keV) concentration profiles in silicon**



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Lehrer et al., IIT 2000 Conf. Proc. IEEE, 695 (2000)

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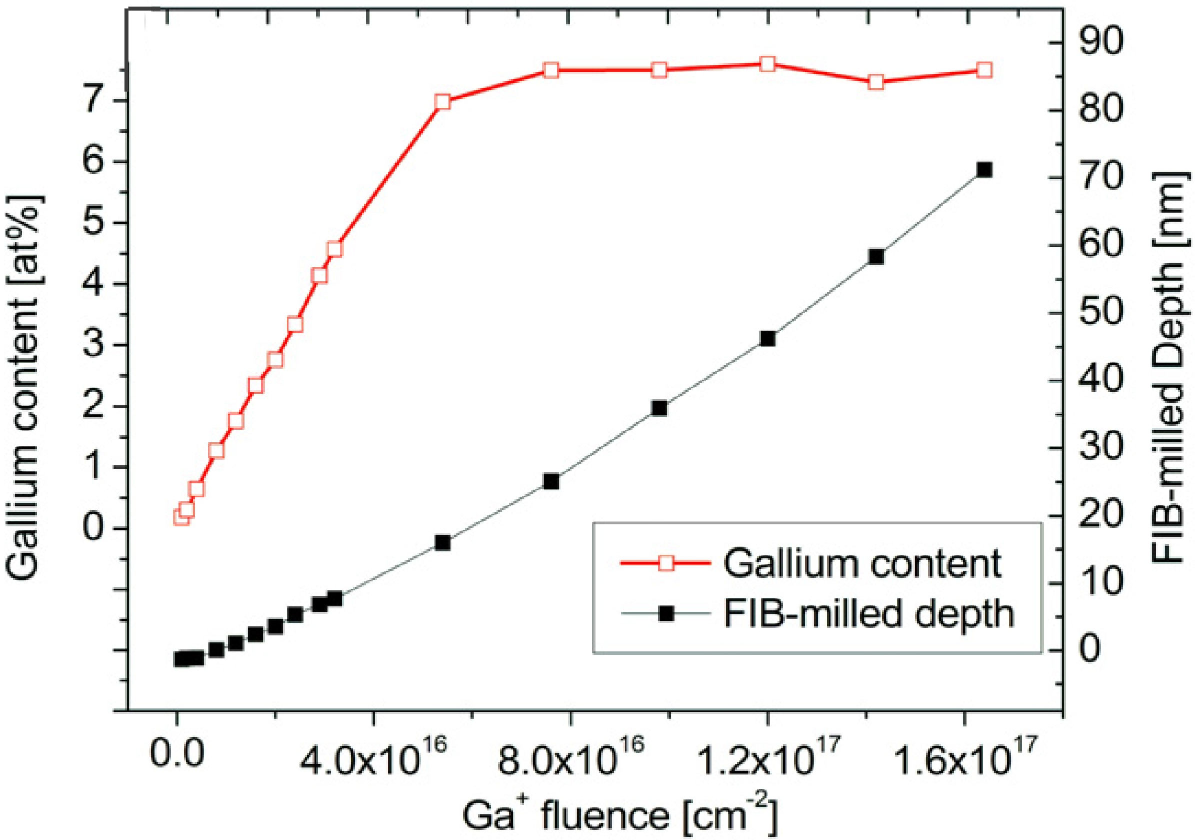

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Roediger et al., Nanotechnology 22, 235302 (2011)

Resistless Ga^+ beam lithography (GaRL)

- Effect that Ga implanted regions show reduced etching rate **in silicon** first published in 1983:
  1. Komuro et al., J. Vac. Sci. Technol. B 1, 985 (1983)
  2. La Marche et al., J. Vac. Sci. Technol. B 1, 1056 (1983)
  3. Berry et al., J. Vac. Sci. Technol. B 1, 1059 (1983)
- All used **wet chemical etching** (H_3PO_4, KOH or NaOH, later also TMAH (*))
- Effect was known before using B implantation and B concentrations > 10^{19} cm^{-3}
- Explanation for B: “surface passivation due to strain effects caused by the impurity atoms” (**)
- At that time, no mechanism identified for Ga implantation
- Today, Ga_2O_3 formation is assumed to provide the masking capability (***)

(*) Sievilä et al., Nanotechnology **21**, 145301 (2010)
(**) Palik et al., J. Electrochem. Soc. **129**, 2051 (1982)
(***) Salhi et al., Nanotechnology **28**, 205301 (2017)

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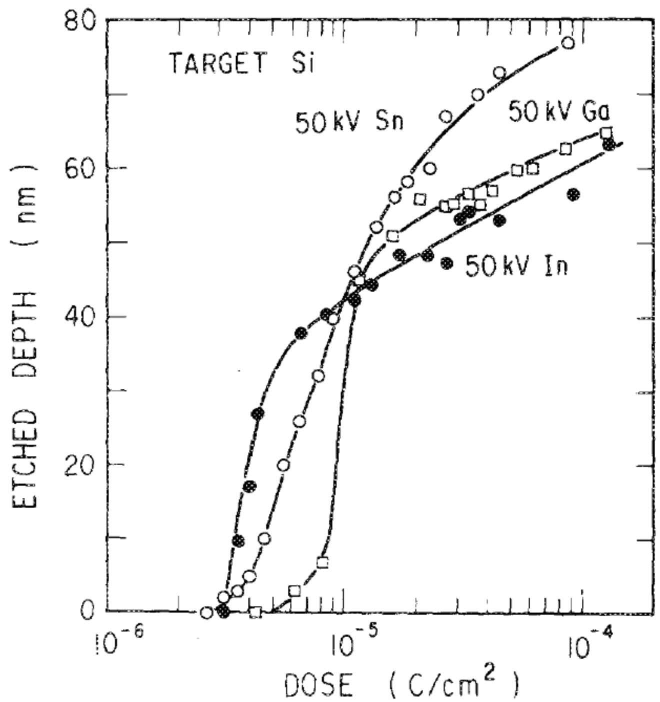
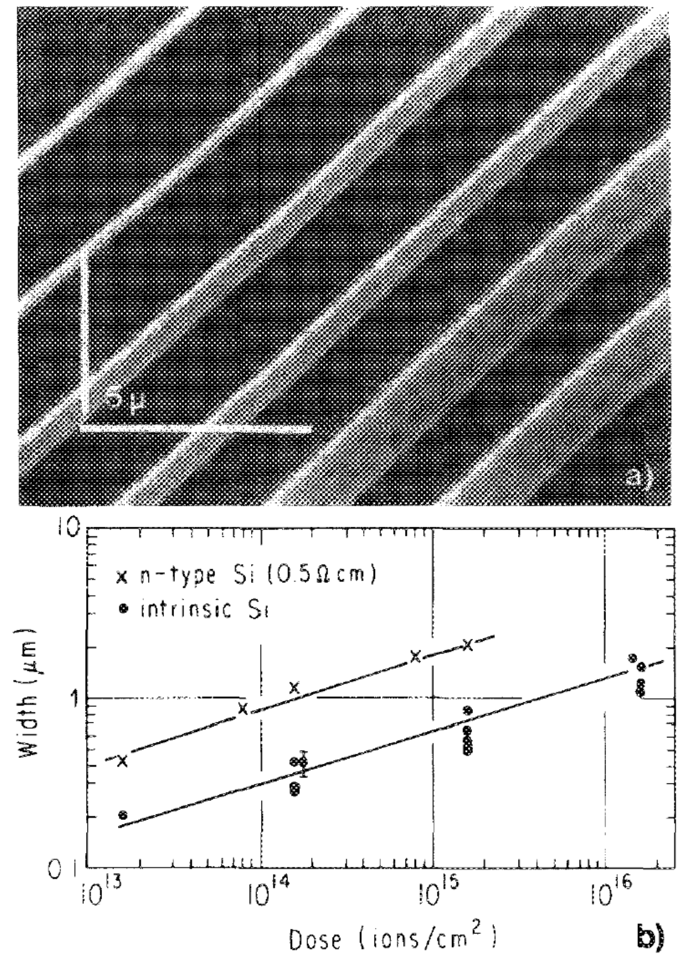


Etched Si depth vs ion dose [1]



Variation of Si linewidth with dose (50wt% NaOH) [2]

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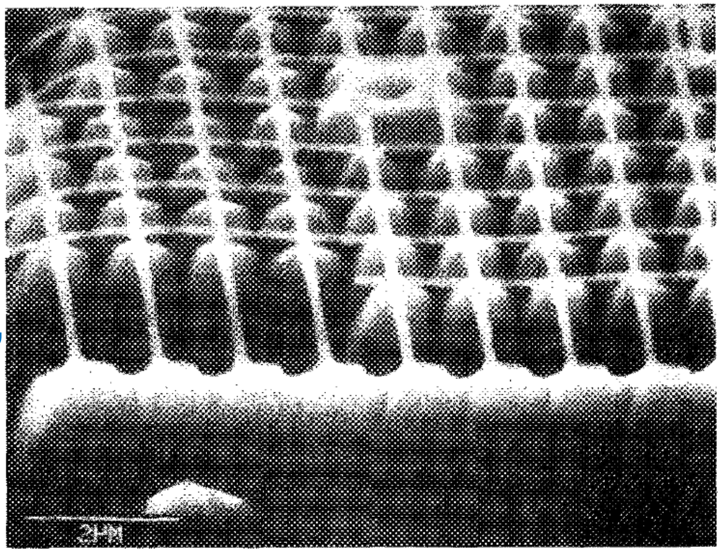
Fully under-etched features → "free-standing"



Ga-doped Si lines (140 nm wide, 20 nm thick) [3]

Resistless Ga^+ beam lithography (GaRL)

- Early publications which show the use of GaRL with subsequent **dry etching (typically reactive ion etching RIE)**:

1. Harriot et al., J. Vac. Sci. Technol. B 7, 1467 (1989) → InP + Cl+Ar etch
2. Akaike et al., Jpn. J. Appl. Phys. 31, L410 (1992) → Nb + CF4
3. Edenfeld et al., J. Vac. Sci. Technol. B 12, 3571 (1994) → Si + SF6/O2
4. Zachariasse et al., Microelectron. Eng. 35, 63 (1997) → Ti + SF6

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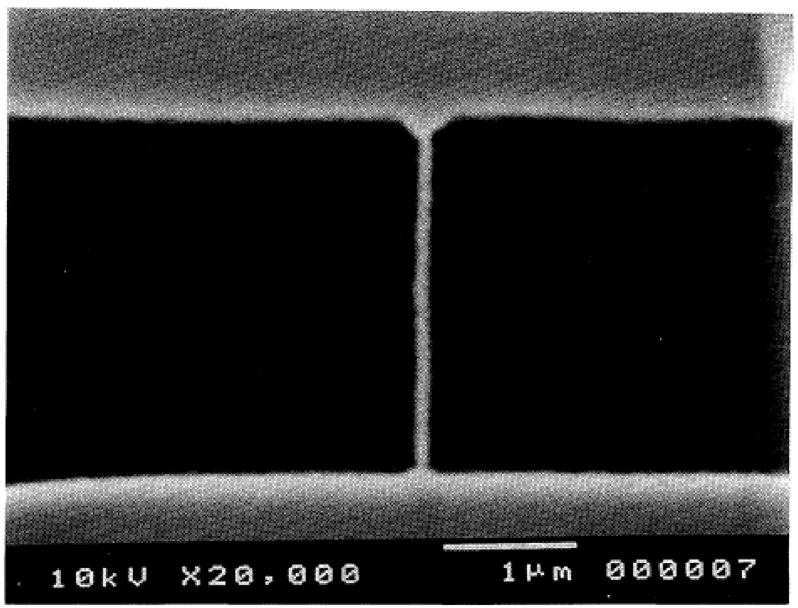

Nb strip (100 nm width, $2.7 \cdot 10^{16}$ 1/cm²) [2]

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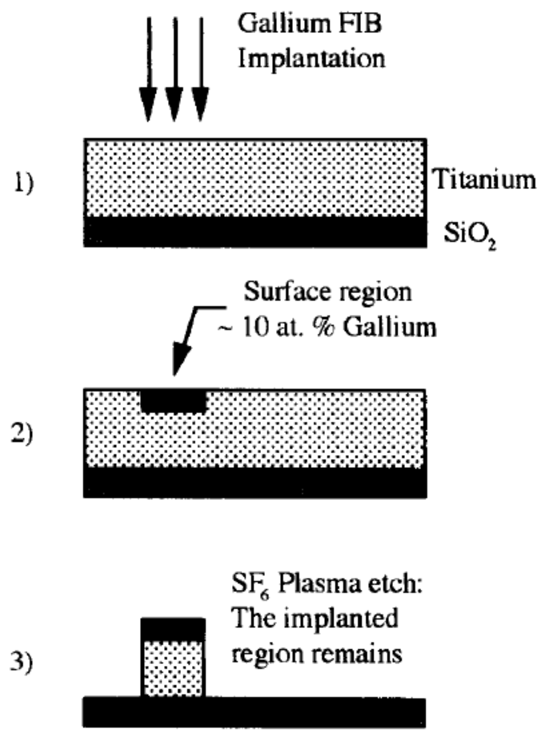

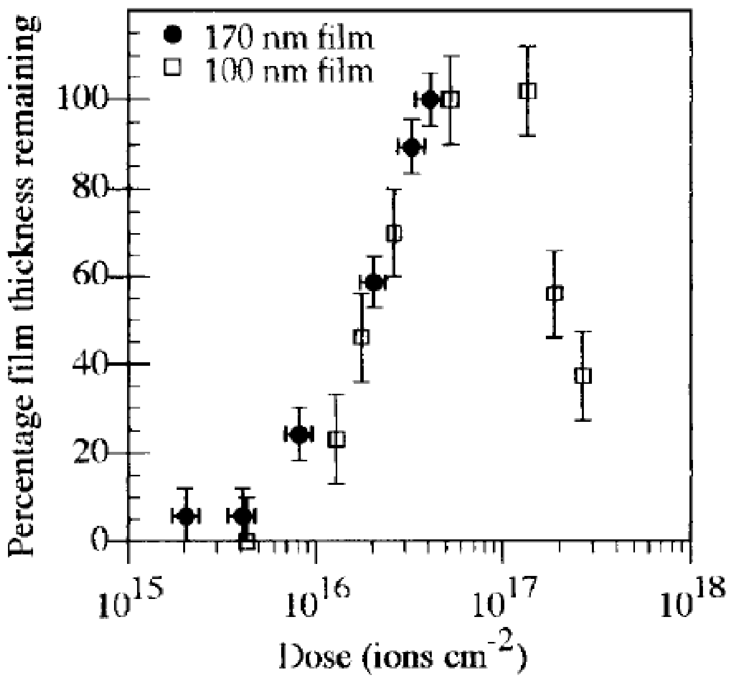

Influence of ion dose on Ti feature height [4]

Resistless Ga^{+} beam lithography (GaRL)

- **GaRL works for many different materials**, among them:
  - Si, InP, Nb, Ti (as shown before)
  - SiO_2: Choquette et al., Appl. Phys. Lett. 62, 3294 (1993)
  - ZnO: Fang et al., Nanotechnology 21, 505703 (2010)
  - Diamond: McKenzie et al., Diamond Relat. Mater. 20, 707 (2011) (*)
  - GaN: Stevens-Kalceff et al., Proc. of SPIE 8766, 87660I (2013) (UV photoelectrochemical etching)
  - Al_2O_3: Liu et al., Nanotechnology 24, 175304 (2013)
  - 4H-SiC: Beuer et al., MNE 2013, London UK
  - Si_3N_4: Erdmanis and Tittonen: Appl. Phys. Lett. 104, 073118 (2014)

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Resistless Ga^+ beam lithography (GaRL)

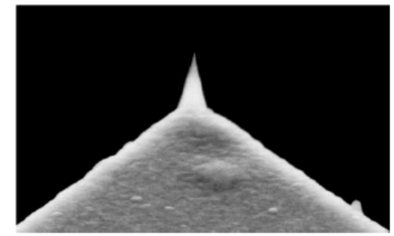
Adama Probe Family – Conductive Diamond

Adama innovations

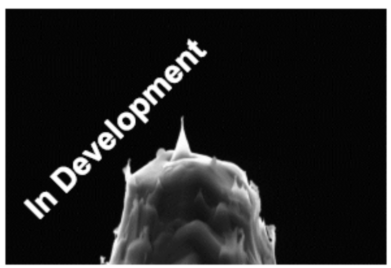
Type 1: "Apex"

Standard Contact or Dynamic Mode

- Diamond
- Tip radius < 7 nm

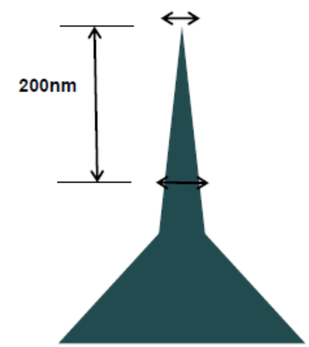


Type 2: "Spire"

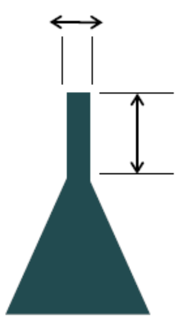


Supersharp

- Conical spikes
- Tip Radius < 5 nm
- Length > 200 nm
- Diameter at 200 nm : < 30 nm

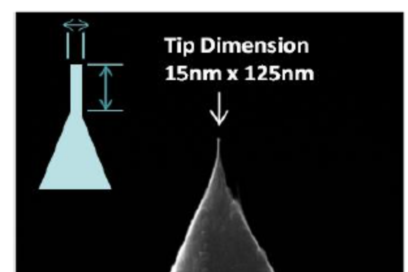


Type 3: "Pillar"



Pillar

- Constant (+/-5 nm) diameter columnar tip
- Rev 1 : 25 nm diameter, > 125 nm length
- Rev 2 : 15 nm diameter, > 125 nm length



Contact : enquiries@adamainnovations.com www.adamainnovations.com

Resistless Ga^+ beam lithography (GaRL)

- **Why does GaRL work (especially for dry etching)?**
  - Some hypotheses were introduced, of which the most relevant **for Si** are:
    - formation of gallium oxides (Ga_2O_3) at sample surface which do not react with etching gases and can only be removed by physical sputtering [1,2]
    - formation of involatile compounds of Ga and substrate material, also in fluorine based chemistry without O_2 such as SF_6/C_4F_8 [3,4]

1 Choquette and Harriot, Appl. Phys. Lett. 62, 3294 (1993)
2 Schmidt et al., J. Electrochem. Soc. 152, G875 (2005)
3 Zachariasse et al., Microelectron. Eng. 35, 63 (1997)
4 Henry et al., Nanotechnology 21, 245303 (2010)

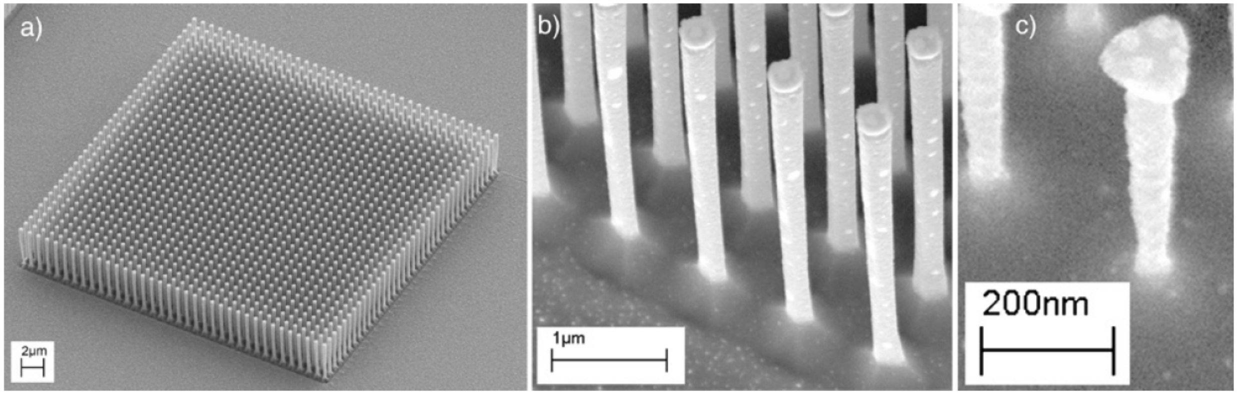
Resistless Ga+ beam lithography (GaRL)

- **Si: Cryogenic or mixed mode etching (DRIE) enables structures with very high aspect ratios (AR) and vertical sidewalls**

AR ~ 10-14

- 120 °C

SF_6/O_2

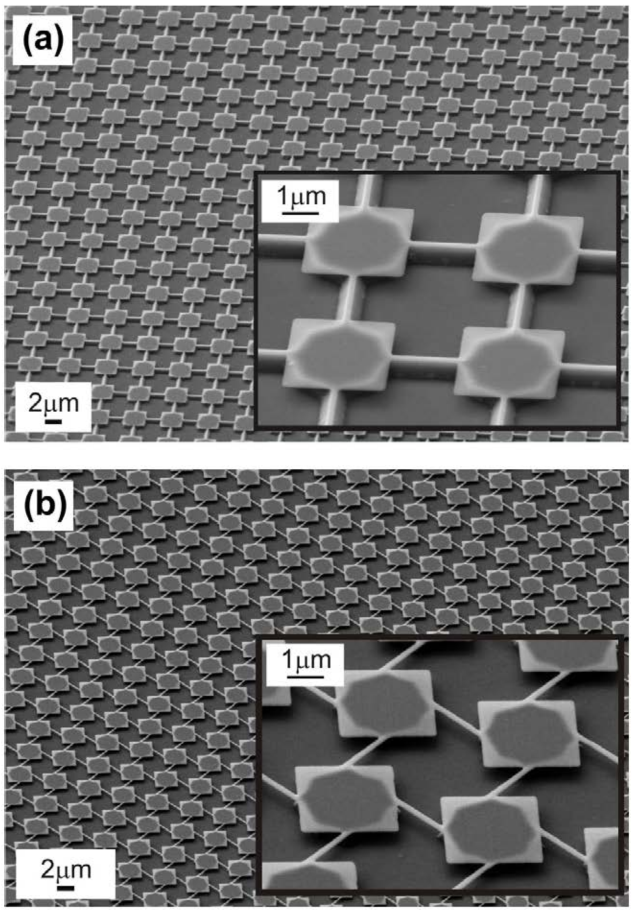


a, b) 280 nm diameter pillars (3 min RIE), c) 65 nm diameter pillar (30 s RIE) *

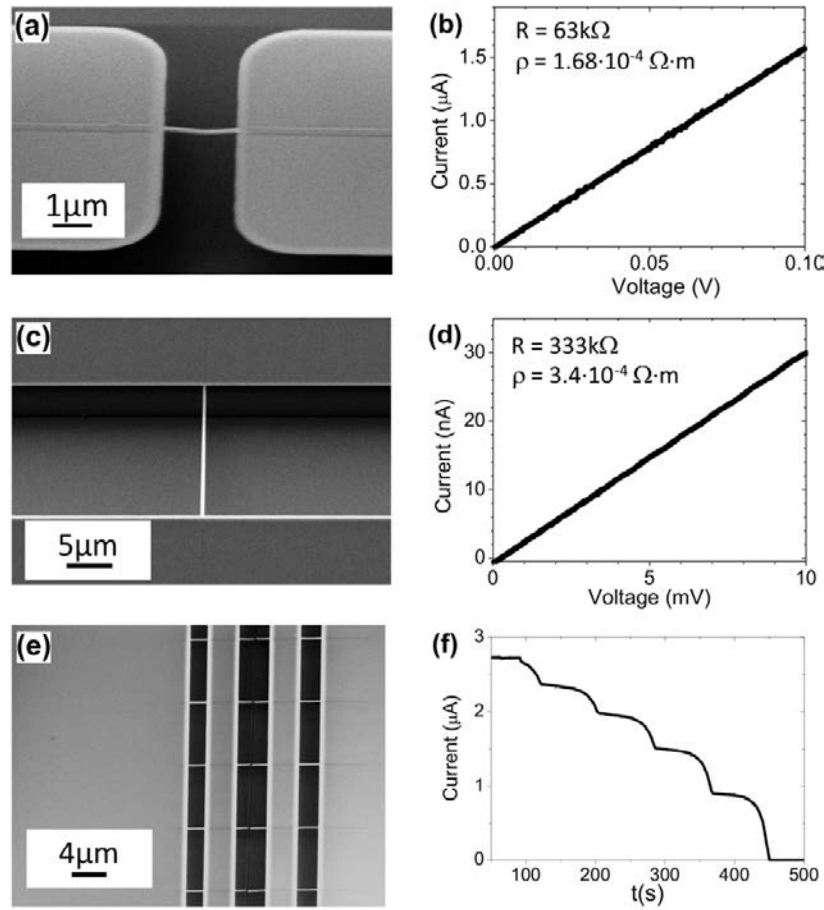
* Cherukov et al., Nanotechnology 20, 065307 (2009)

Resistless Ga^+ beam lithography (GaRL)

- **Si: CMOS compatible suspended structures for nano-mechanical devices**
- TMAH wet etching, annealing at T > 600 °C in N_2 to remove Ga (plus B doping)



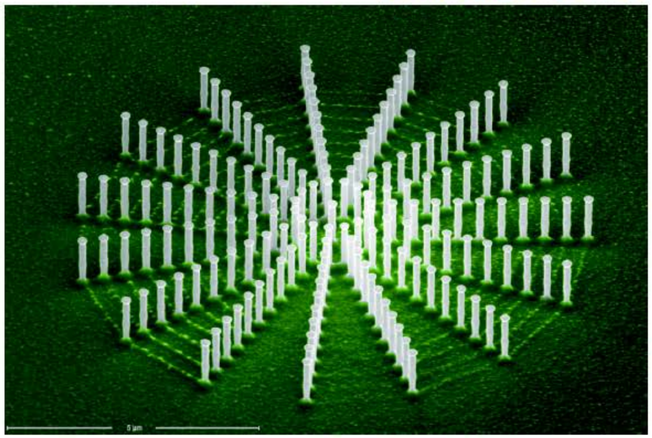
Llobet et al., Nanotechnology 25, 135302 (2014)

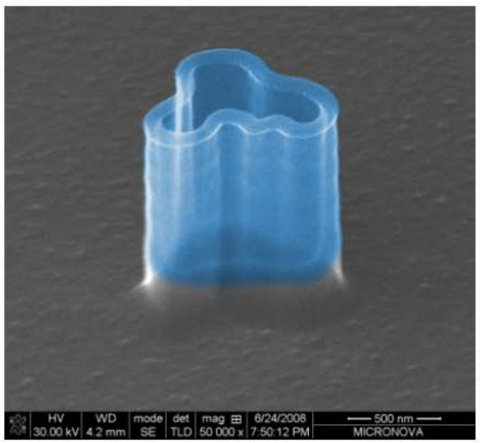


Resistless Ga$^+$ beam lithography (GaRL)

- **Ilkka Tittonen , FOR3NANO, 28.-30.06.2017, Helsinki, Finland**

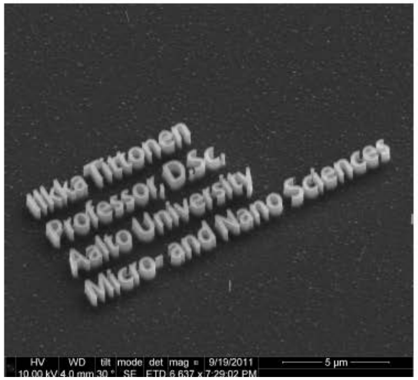
Science Meets Art in Micronova

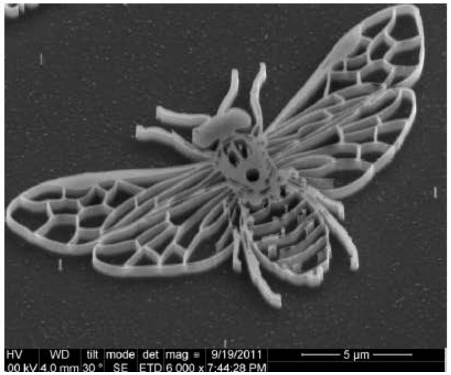




- "Science as Art":
  1. Prize in MRS Spring Meeting 2008 competition in San Fransisco

- The smallest Aalto vase
  (N. Chekurov, Department of Micro and Nanosciences)





Outline

- Introduction
  - Resistless Ga^+ beam lithography
- **Experimental @ IISB**
  - Sample processing
  - Results for Si, SiO_2 and 4H-SiC
- Summary

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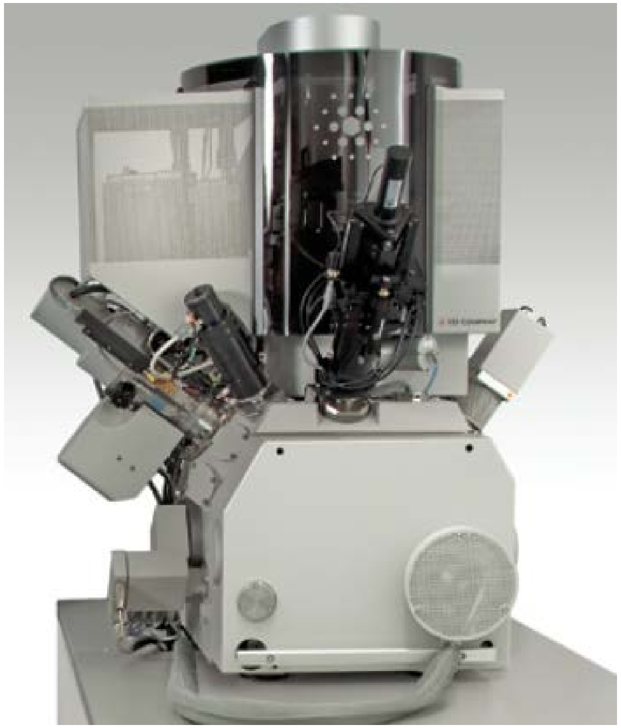
Sample processing



Helios Nanolab 600
Image: FEI

- **Samples**
  - always small pieces were used
    - 4 cm² p(Boron)-doped **Si**
    - (12.5 mm)² **quartz** pieces
      → covered with thin conductive C layer
    - 1 cm² **4H-SiC** highly n(Nitrogen) doped substrates

- **Resistless Ga^+ beam lithography**
  - FEI Helios Nanolab 600: 30 keV, 28 pA / 17 nm (and 280 pA / 31 nm for SiO_2)
  - squares, circles, lines, pyramids…
  - doses ranging from $1 \cdot 10^{15}$ to $1 \cdot 10^{19}$ cm^{-2}

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Sample processing – RIE

- **RIE tools**: lab tool usage → used for various processes
  - STS Multiplex ICP for Si and SiO_2
  - Oxford Instrument PlasmaPro 100 for 4H-SiC

- Si: mixture of SF_6 and C_4F_8
- SiO_2: mixture of C_4F_8 and O_2
- 4H-SiC: mixture of SF_6 and O_2

- variation of gas composition, temperature (10-20 °C), pressure, coil and platen power

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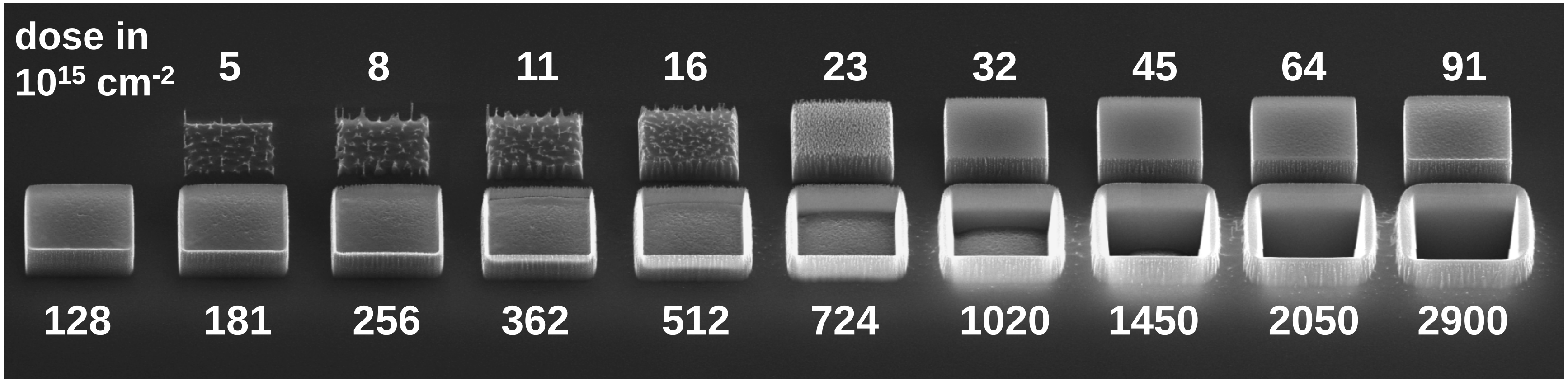
Results for silicon

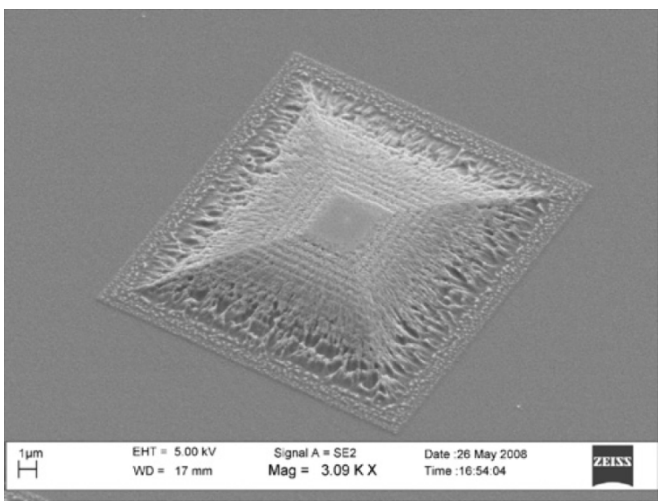
- **Etch mask capability of FIB irradiated areas**
  - squares of 1.5*1.5 µm²
  - threshold dose required for masking (typically around $1\text{-}3\cdot10^{15}$ cm^{-2})
  - quite rough surfaces for low dose masking
  - nearly optimum masking and surfaces for certain dose range (here: $3\text{-}7\cdot10^{16}$ cm^{-2}, structure height: 550 nm)
  - FIB sputtering for doses above appr. 10^{17} cm^{-2}



Rommel et al., Microelectron. Eng. 110, 177 (2013)

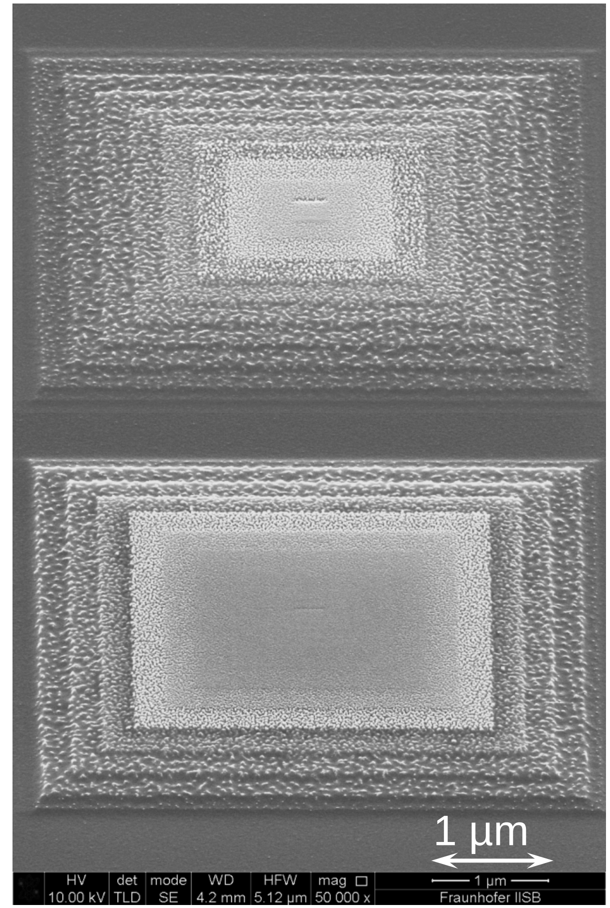
Results for silicon

- Rough surfaces for low dose masking
  → defined smooth 2.5D/3D structures
  hardly possible?
- Example: different pyramids



Example from literature *

patterning time: 10.8 s
dose step: ≈ $1.9 \cdot 10^{15}$ cm^{-2}



patterning time: 14.3 s
dose step: ≈ $2.5 \cdot 10^{15}$ cm^{-2}

Rommel et al., Microelectron. Eng. 110, 177 (2013)

* Chekurov et al., Nanotechnology 20, 065307 (2009)

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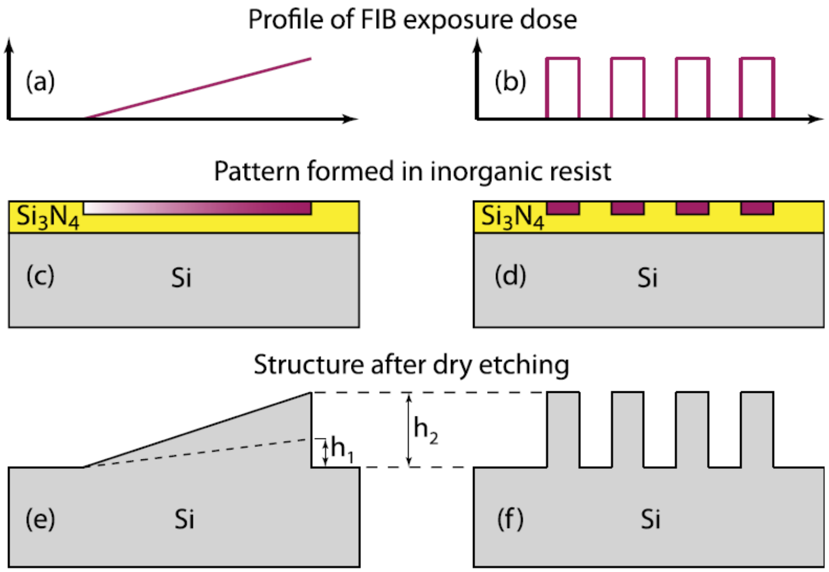
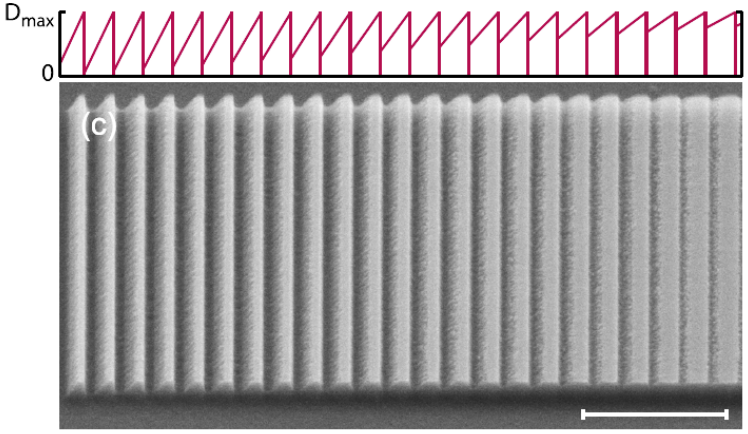
2.5D structures with appropriate hard mask

- **Use of Si_3N_4 together with optimized (but slow) etching process (pure CF4)**



Scheme for hard mask GaRL greyscale patterning

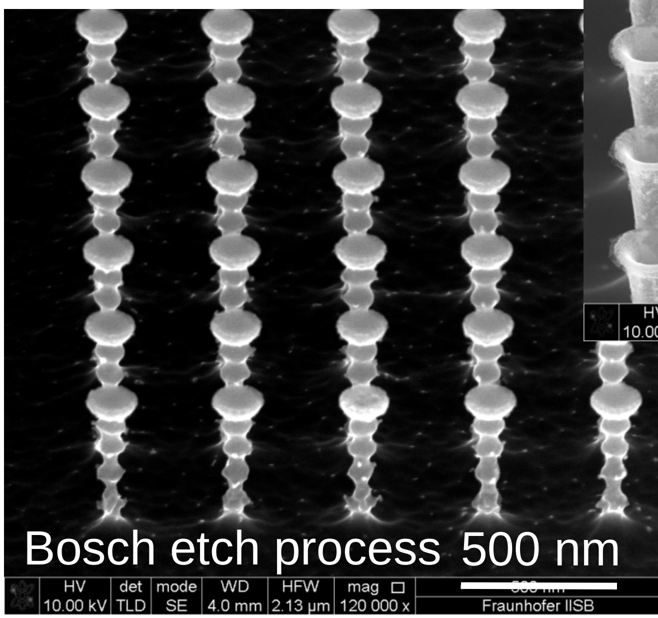


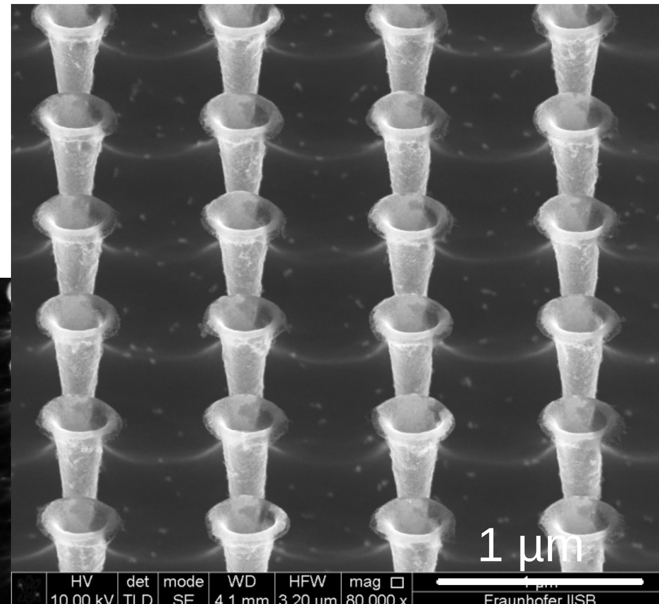
Example of blazed gratings
(period and height: 200 nm):
scale bar: 1 µm

Erdmanis et al., Appl. Phys. Lett. 104, 073118 (2014)

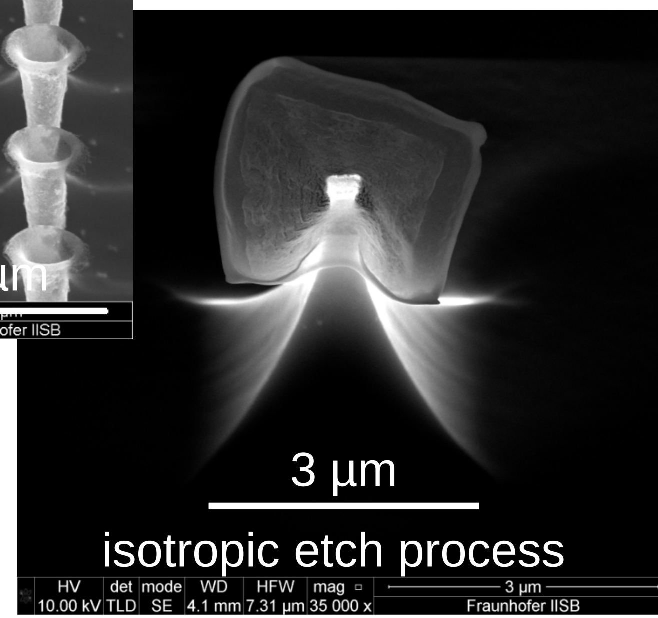
Results for silicon

- **Influence of RIE and FIB process parameters**





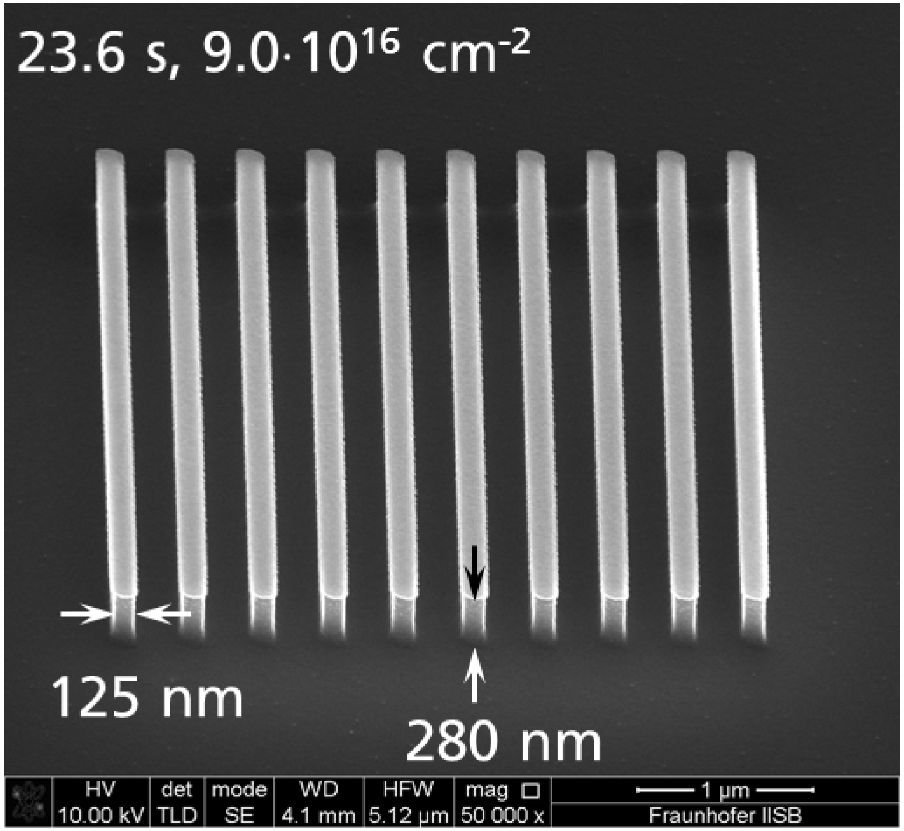
very high ion dose

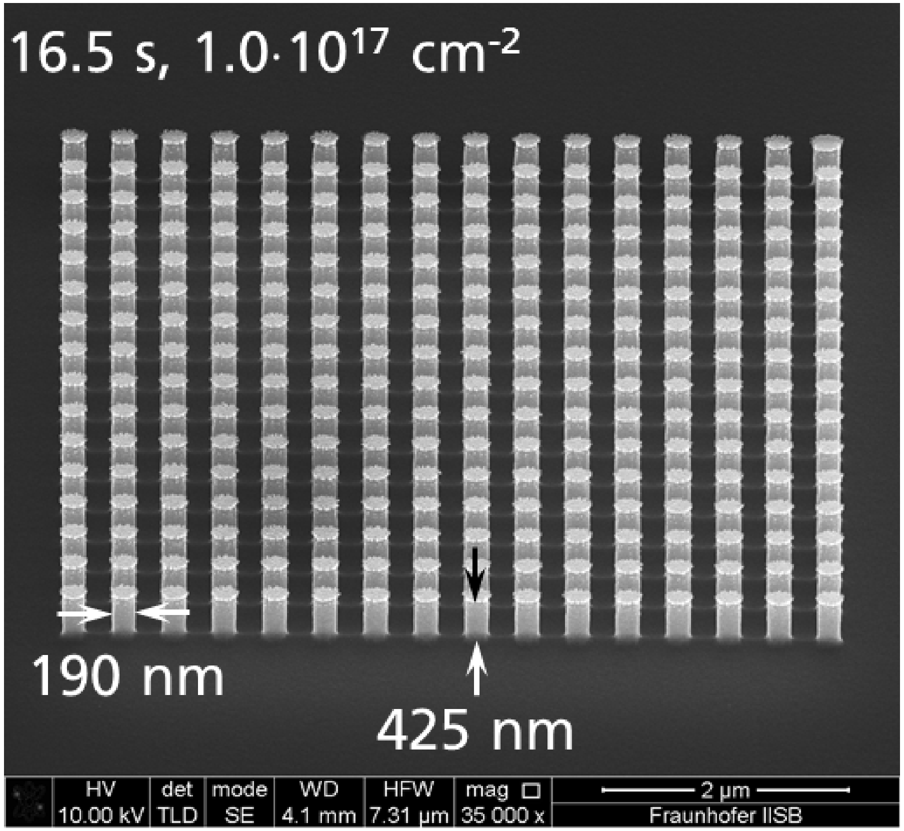


Rommel et al., Microelectron. Eng. 110, 177 (2013)

Results for silicon

- **Results for lines and pillars**





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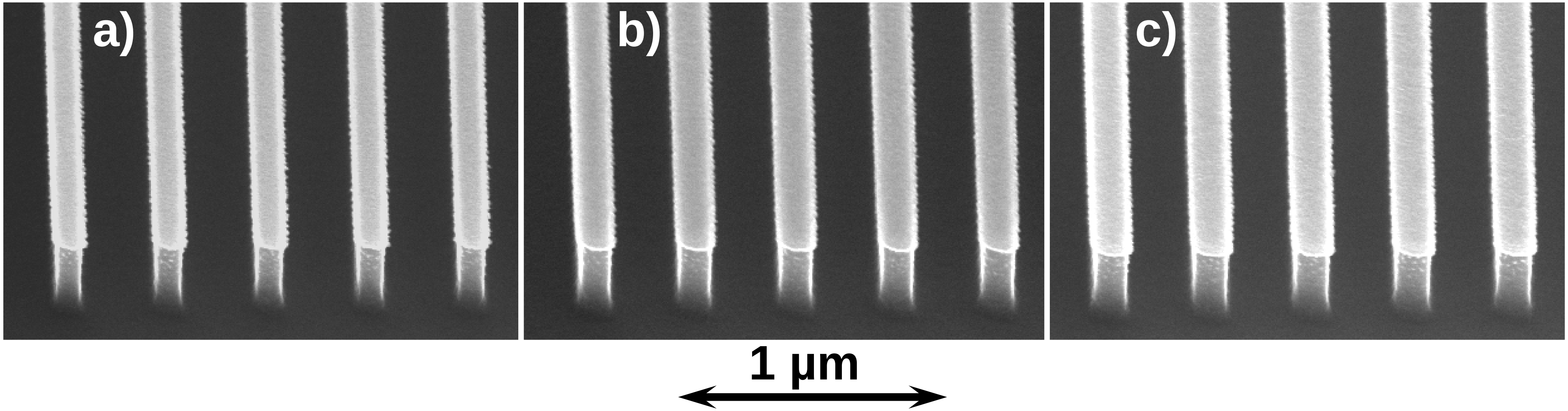
Results for silicon

- **Influence of dose on pattern width**
- 2.5 min RIE (10°C chuck temperature), height of lines: 320 nm



	dose in cm^{-2}	line width in nm
a)	$5 \cdot 10^{16}$	105
b)	$9 \cdot 10^{16}$	140
c)	$1 \cdot 10^{17}$	145

Rommel et al., Microelectron. Eng. 110, 177 (2013)

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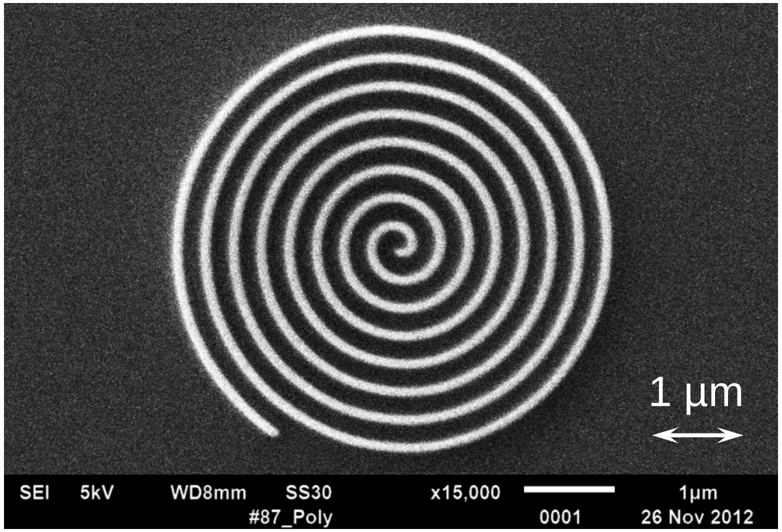
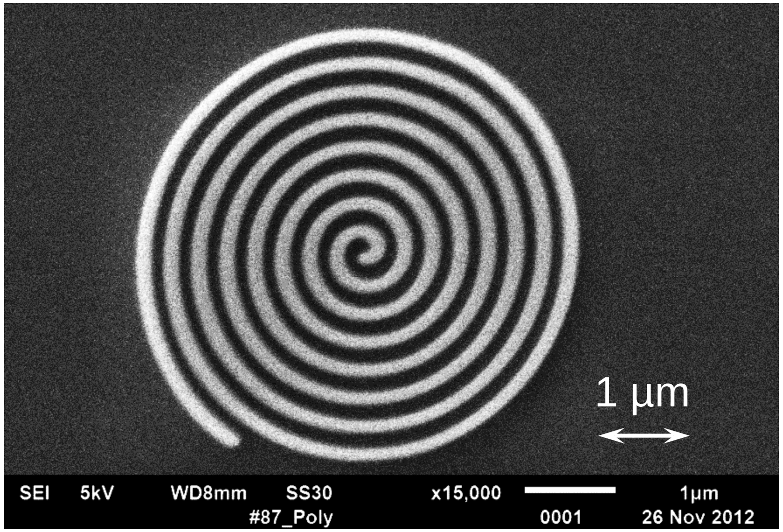
Results for silicon

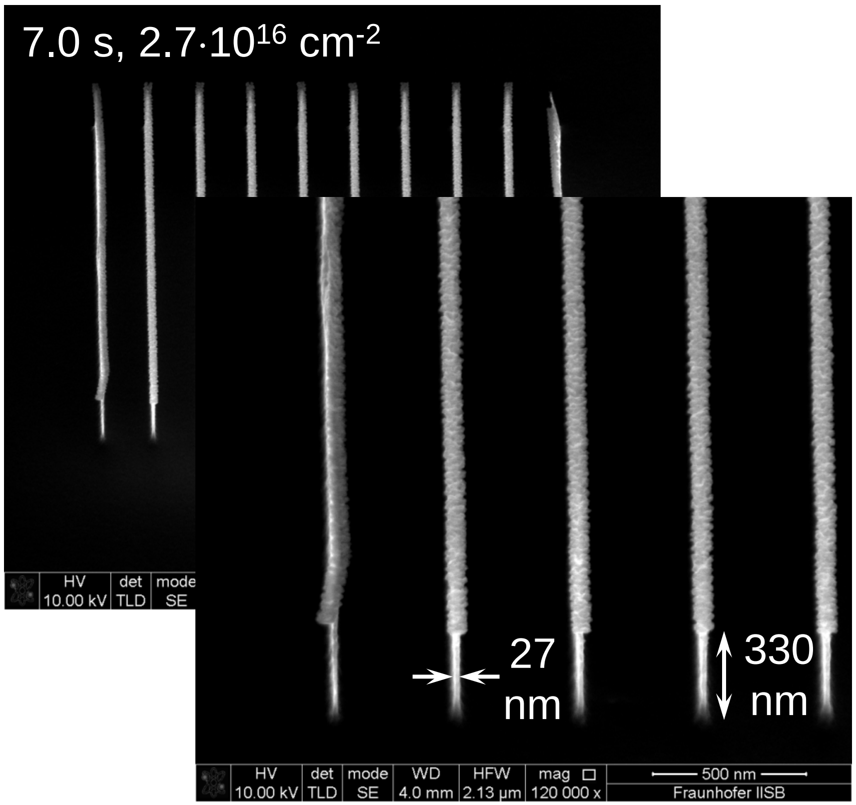
- **Influence of dose on pattern width**
- left: $4 \cdot 10^{16}$ cm^{-2}, right: $1 \cdot 10^{17}$ cm^{-2}

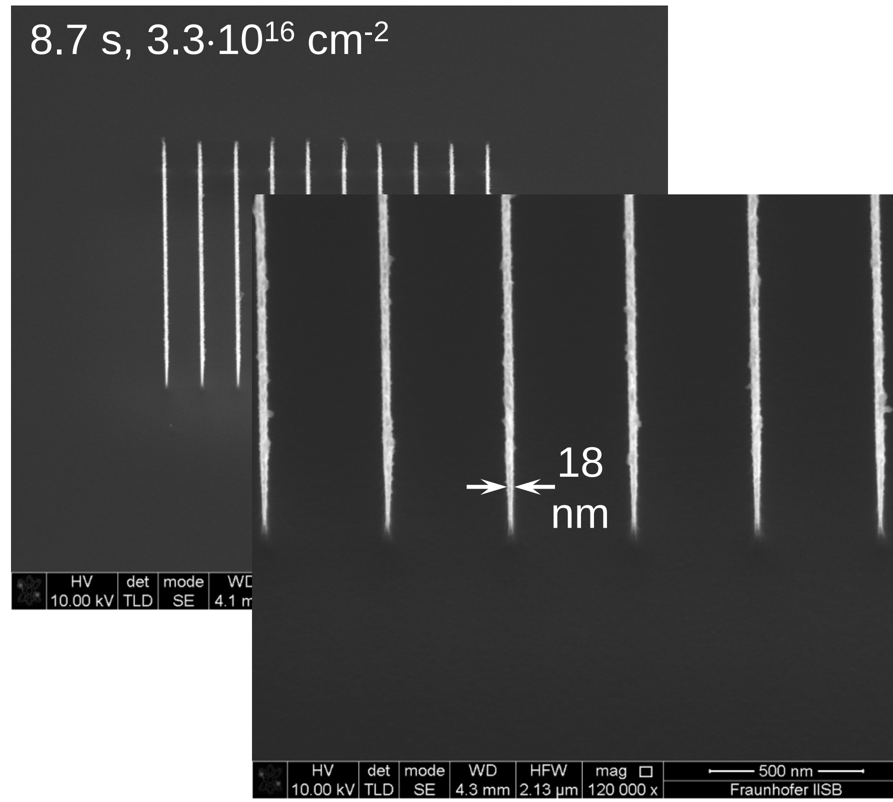




Results for silicon

- **Resolution of lines (array of 10 lines , 4.1 µm length)**

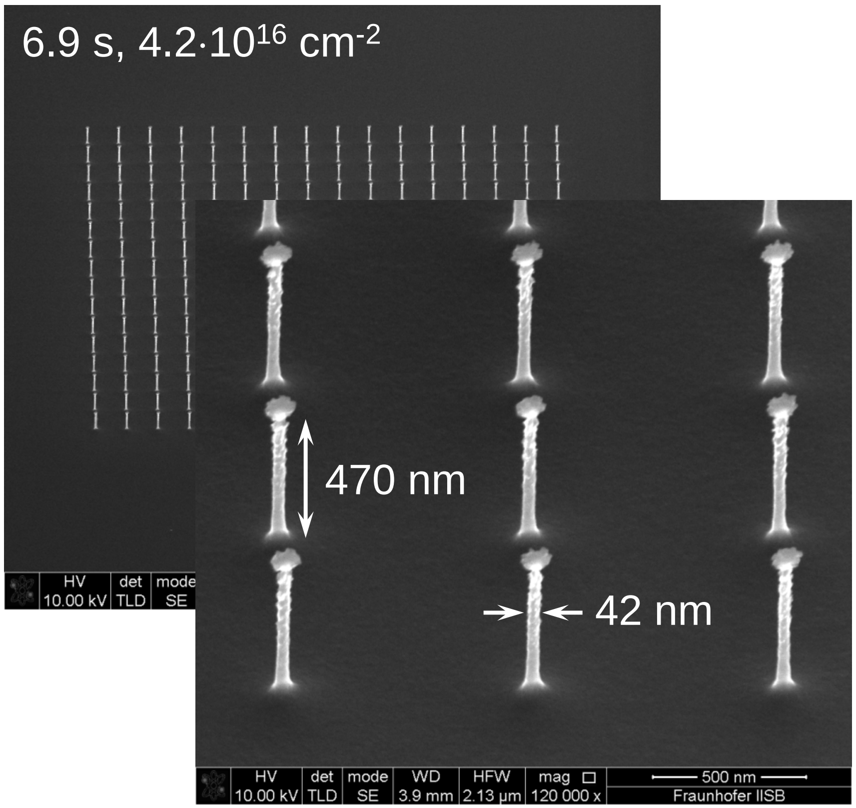


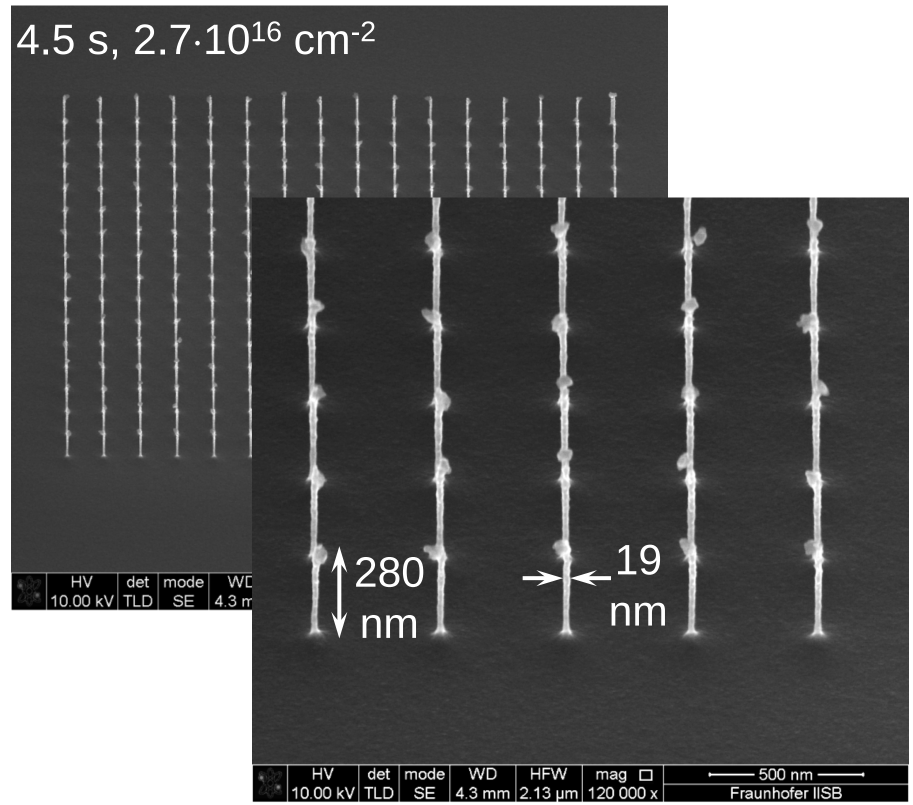


Rommel et al., Microelectron. Eng. 110, 177 (2013)

Results for silicon

- **Resolution of pillars (array of 16 * 16 pillars)**

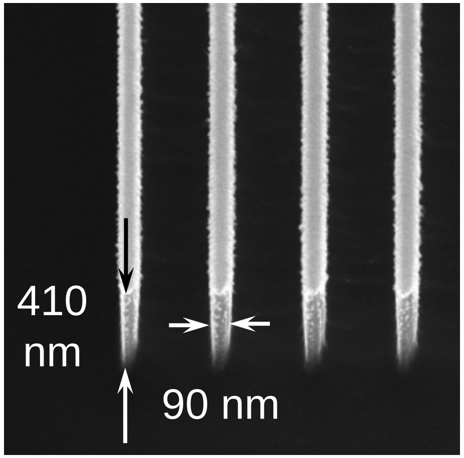




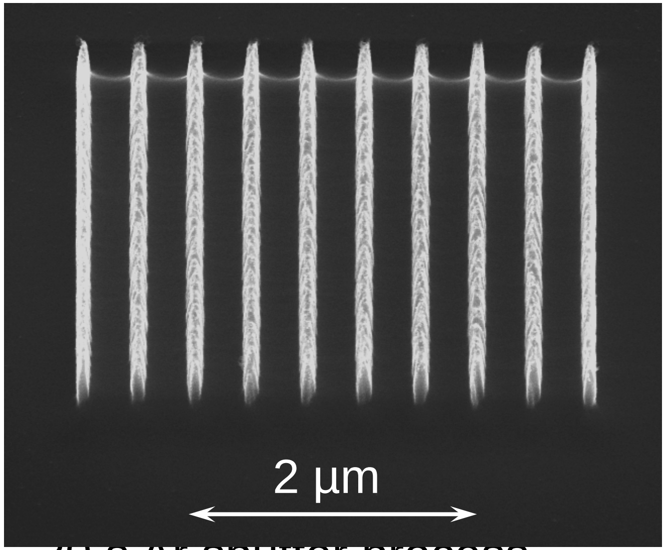
Rommel et al., Microelectron. Eng. 110, 177 (2013)

Results for silicon

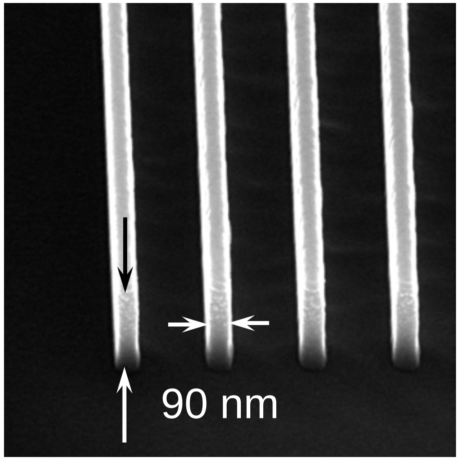
- **Mask removal**
- Approaches
  - RIE until mask is removed → very small process window, rough surfaces
  - Ar sputter process (CS900S VON ARDENNE: 500W, 5µbar, 70sccm Ar)



FIB: $5 \cdot 10^{16}$ cm^{-2},
RIE: 3.5 min



30 s Ar sputter process



60 s Ar sputter process

Rommel et al., Microelectron. Eng. 110, 177 (2013)

Results for silicon

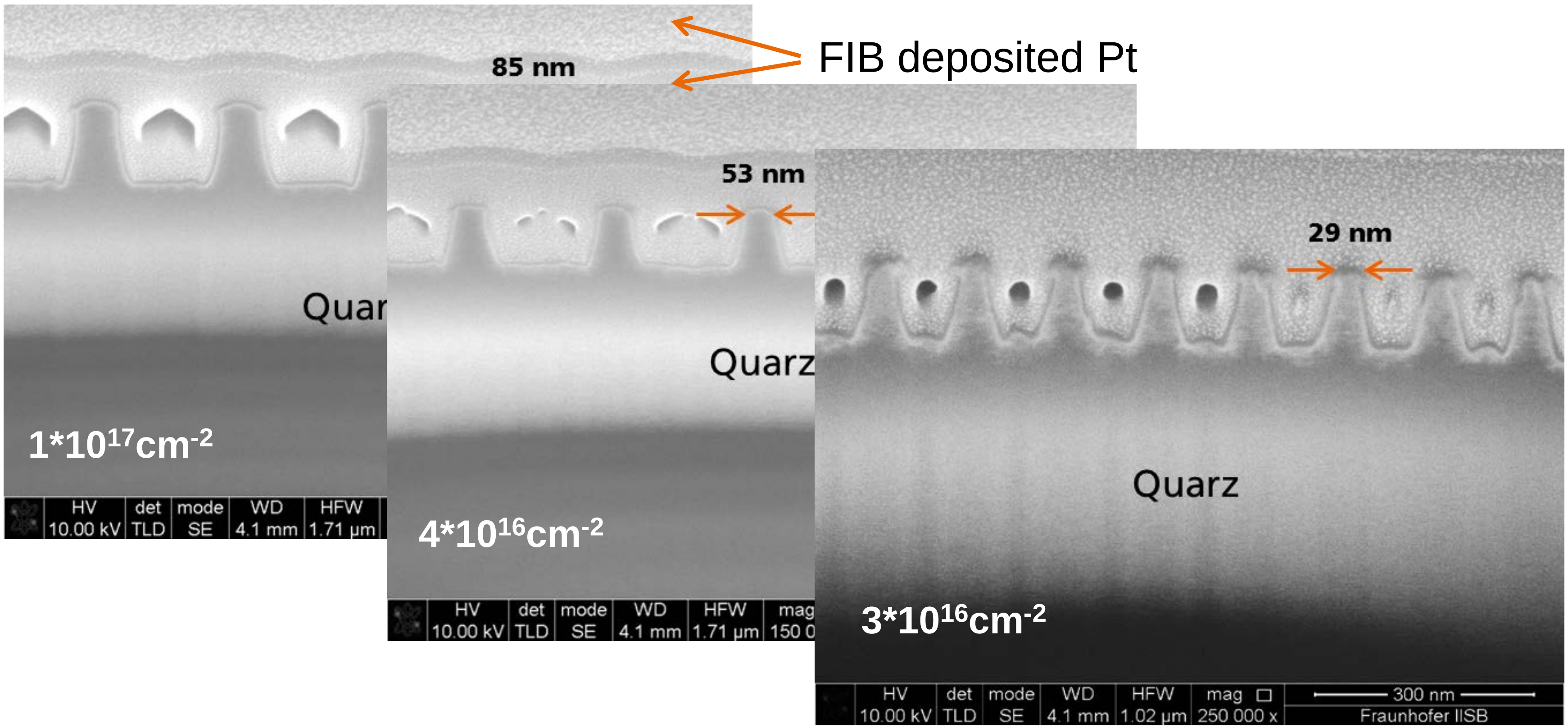
- **Mask removal**
- Approaches
  - RIE until mask is removed → very small process window, rough surfaces
  - Ar sputter process

- Approaches from literature
  - Sample heating to > 600 °C (→ cross contamination → sample deterioration) [1]
  - KOH/H_2O_2 etching [2]
  - Alternatively, hard mask patterning and subsequent hard mask removal [3,4]
    → Ga contamination of target material avoided

1 Llobet et al., Nanotechnology 25, 135302 (2014)
2 Han et al., Nanotechnology 26, 265304 (2015)
3 Ermanis et al., Nanotechnology 25, 335302 (2014)
4 Liu et al., Nanotechnology 28, 085303 (2017)

Results for SiO_2

- **In principle, very similar results for SiO_2 (compared to silicon)**
- Influence of feature size on ion dose → cross sections through lines

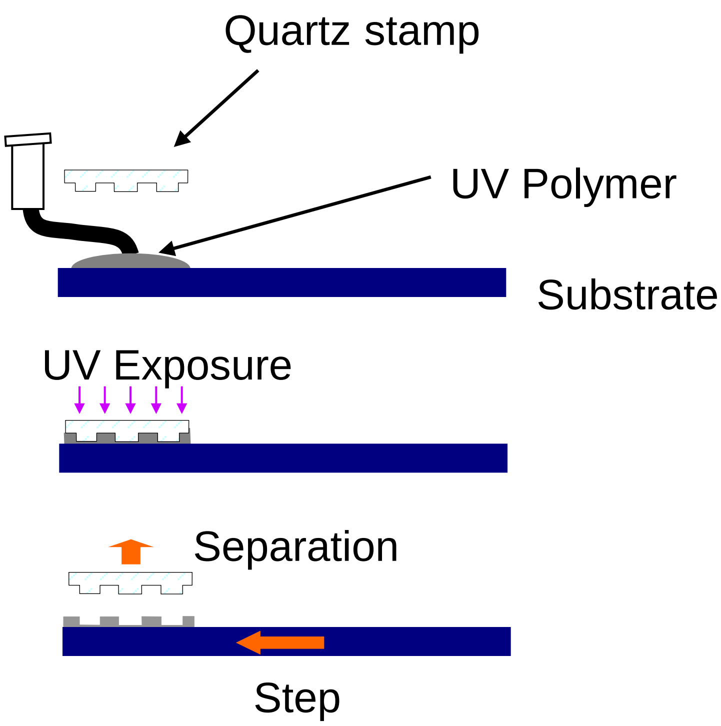


Rumler et al., Nanotechnology 24, 365302 (2013)

Fraunhofer IISB

UV-NIL Step&Repeat imprint process

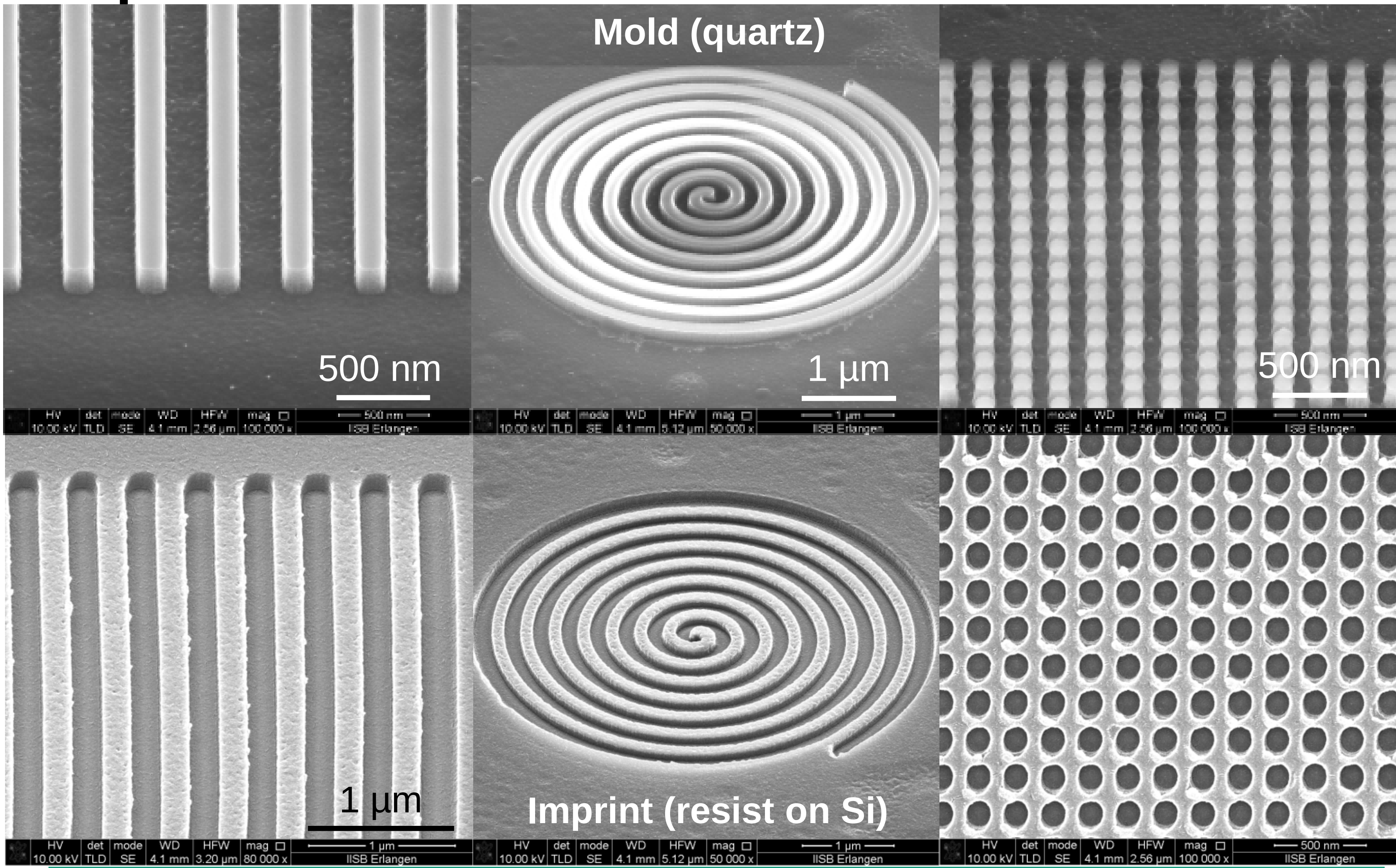
- NPS 300 SET, France
- UV-curable polymer resist mr-UVCur06, mrt, Germany
- Antisticking layer (FDTS) for defect free separation of imprint stamp and resist by Molecular Vapor Deposition (MVD)



Scheme of UV-NIL process

Mathias Rommel

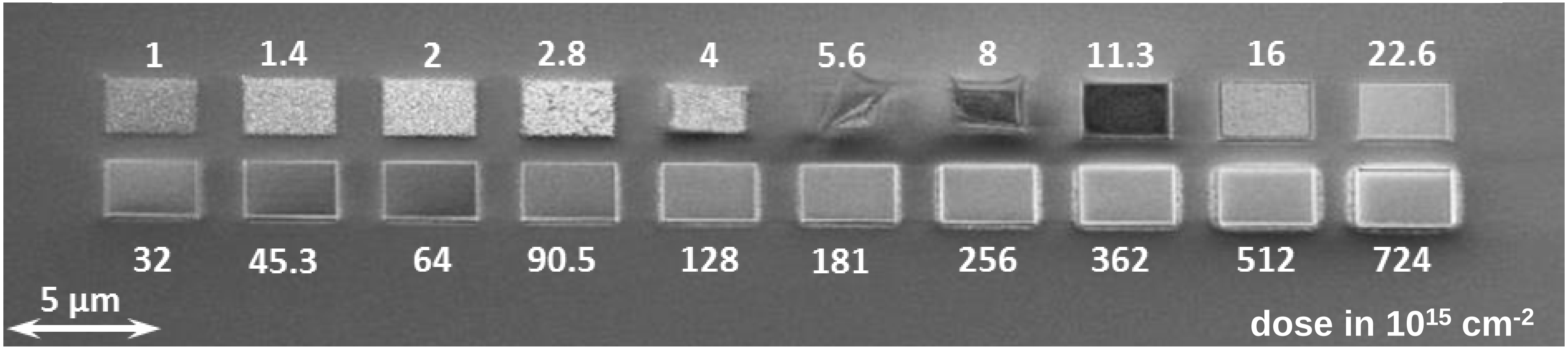
Imprint results



Rumler et al., Nanotechnology 24, 365302 (2013)

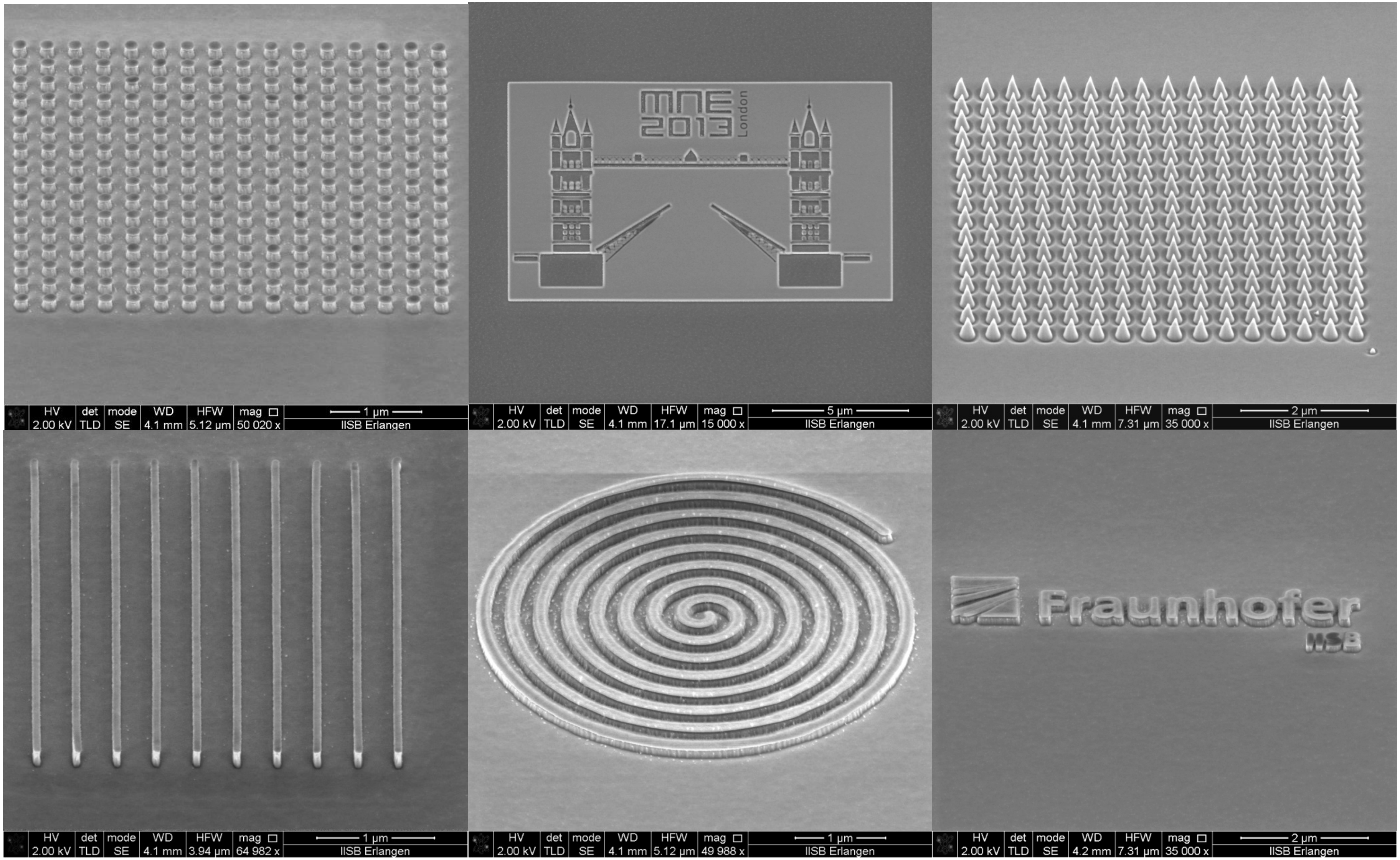
Results for 4H-SiC

- **Etch mask capability of FIB irradiated areas**
  - again, in principle, similar results can be obtained for 4H-SiC
  - threshold dose required for masking (typically around $1 \cdot 10^{15}$ cm^{-2})
  - quite rough surfaces for low dose masking
  - nearly optimum masking and surfaces for a dose range of $2\text{-}7 \cdot 10^{16}$ cm^{-2}



Beuer et al., MNE 2013

Results for 4H-SiC



Beuer et al., MNE 2013

Summary

- Compared to FIB milling, direct resistless Ga^+ beam lithography enables
  - + patterning of larger areas
  - + smaller feature sizes
  - + different feature geometries
  - – less flexible choice of sample material
  - – usually no direct 2.5D structures
- Obtained results show that
  - suspended features can be fabricated both, by wet and dry etching
  - high aspect ratio structures can be obtained
  - even more flexibility can be obtained with high dose FIB irradiation or two step approaches using hard mask patterning by GaRL
  - few approaches for Ga removal are available

Fraunhofer IISB

Thank you for your attention!